Activation and discovery of earth-abundant metal catalysts using sodium tert-butoxide

Activation and Discovery of Earth-Abundant Metal Catalysts Using Sodium *tert*-Butoxide

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Abstract

Catalysis enables the advancement of society by underpinning modern chemical manufacture, academic discovery, materials science and pharmaceutical innovation. The future of catalysis lies in first-row, low toxicity, inexpensive, earth-abundant metals, which one day will supplant precious metals. Iron and cobalt catalysts are emerging as potential precious metal alternatives for alkene and alkyne hydrofunctionalisation reactions. However, these require the use of air- and moisture-sensitive catalysts and reagents, which limits both adoption by the non-expert as well as applicability, particularly in industrial settings. Here we report a simple method for the use of earth-abundant metal catalysts by general activation with sodium *tert*-butoxide. Using only air- and moisture-stable reagents and catalysts, both known and, significantly, novel catalytic activity have been successfully achieved. This activation method allows for the easy use of earth-abundant metals, including; iron, cobalt, nickel and manganese, and represents a generic platform for the discovery, application and commercialisation of non-precious metal catalysis.

Introduction

Earth-abundant metal catalysis is key to the sustainable future of chemical synthesis and manufacturing. Despite this, precious metal catalysts remain the go-to for both industry and academia. Several reductive strategies have been developed to enable state-of-the-art earth-abundant metal catalysis, however the majority of these rely on the use of air- and moisture-sensitive pre-catalysts (Figure 1, **a**)[1-8] or reagents (Figure 1, **b**)[9-22] which are challenging to handle, store and transport, and thus hinder widespread adoption of these otherwise powerful methods. In the ideal scenario, all reagents and pre-catalysts would be air- and moisture-stable solids that are easily handled, and applicable in large-scale processes with minimal associated hazards. With this in mind, we questioned whether a *non-organometallic* reagent could serve as a pre-catalyst activator, greatly simplifying low-oxidation state non-precious

metal catalysis. This paper describes what promises to be a significant step along that road; the universal activation of first-row transition metal pre-catalysts using sodium *tert*-butoxide (Figure 1, **c**).

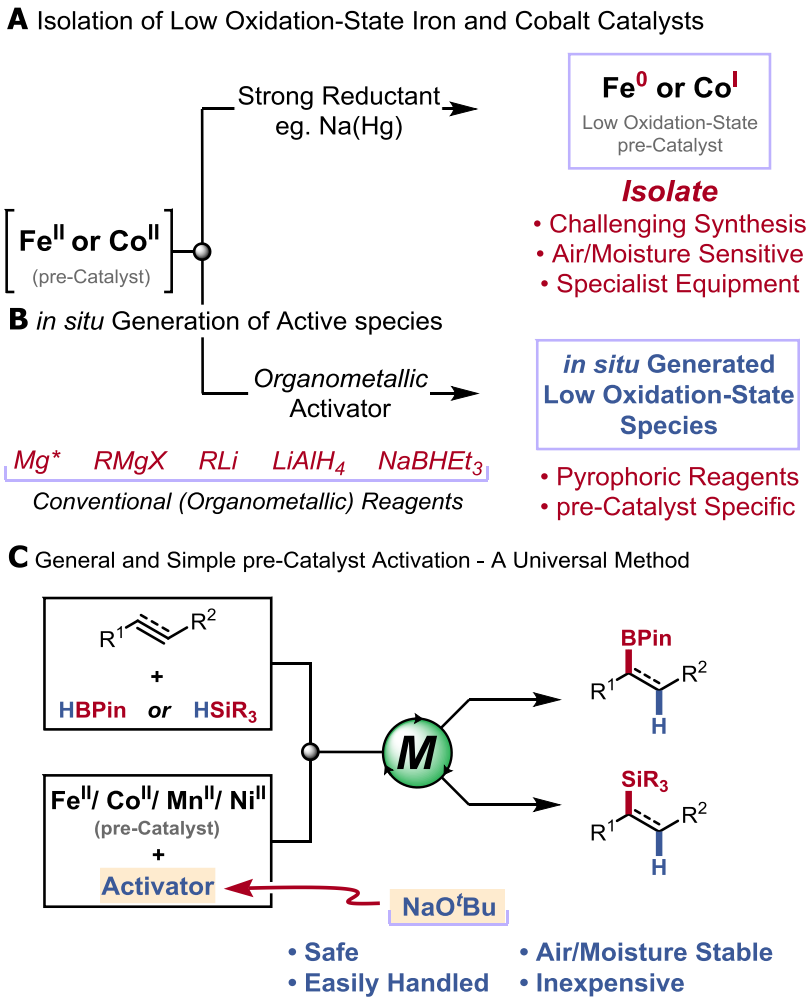


Figure 1 | **Activation strategies for iron and cobalt pre-catalysts. a**, Typical routes to generate catalytically active iron(0) and cobalt(I) catalysts. **b**, Analogous iron(II) and cobalt(II) complexes are bench-stable surrogates for these low-oxidation state species, which are 'activated' using external organometallic reagents or reducing metals as *in situ* reductants. **c**, Organometallic-free *in situ* pre-catalyst activation for olefin hydroboration and hydrosilylation using first-row transition metals.

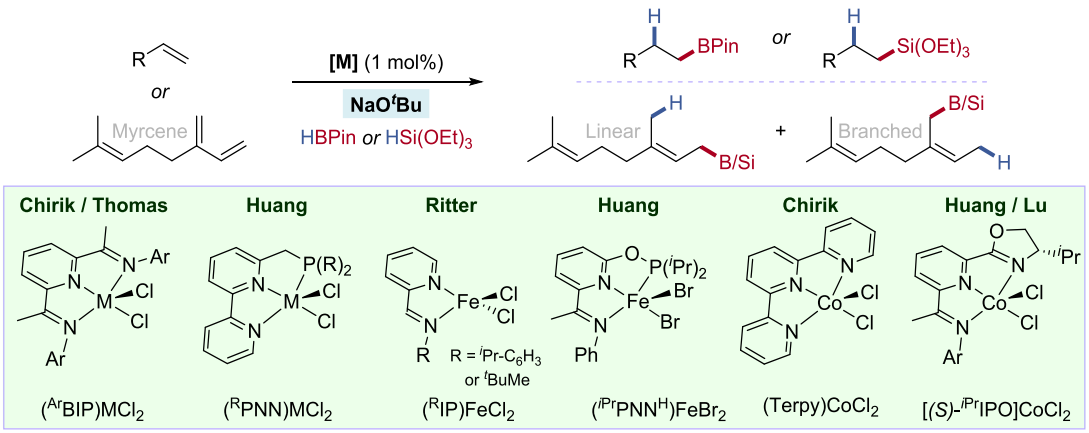
In an effort to discover a practical pre-catalyst activation method we first targeted iron-catalysed hydroboration as there are established benchmarks using both a state-of-the-art isolated 'Fe(0)' catalyst[9] and an organometallic activation method[18]. After testing several reagent classes, metal alkoxide salts proved to be exceptionally efficient activators (See SI, Table S1). An important series of control reactions established that the combination of iron(II) pre-catalyst and sodium *tert*-butoxide was

necessary for any catalytic activity. Stoichiometric quantities of alkoxide salt have been previously used to activate $B_2(Pin)_2$ and transfer *B(Pin)* to iron(II) chloride, but not to trigger low oxidation-state catalysis or a general reductive catalysis platform[19]. From a practicality perspective it is key to note that these reactions were conducted using reagents as supplied from commercial vendors, without purification, even after extended storage in air, and using a single straightforward activation protocol.

Results and Discussion

The generality of any synthetic protocol is essential for widespread adoption. Therefore it was important to assess if the NaO^{t}Bu activation could be applied to a range of pre-catalyst classes (Table 1). Chirik has reported the use of iron(0) bis(imino)pyridine complexes as catalysts for the hydroboration of alkenes, where the key iron(0) species is prepared by sodium-mercury amalgam reduction of the iron(II) precursor[9]. NaO^{t}Bu activation of the bench-stable iron(II) pre-catalyst ^{Et}BIPFeCl$_2$ gave the linear alkylboronic ester product in excellent yield (>95%) with complete control of regioselectivity, and, importantly, equalling the reactivity of the isolated iron(0) manifold (Table 1, entry 1a) and surpassing that using an organometallic reagent (Table 1, entry 1b). Ethyl magnesium bromide (EtMgBr) has also been used for the *in situ* activation of the iron(II) pre-catalyst ^{Et}BIPFeCl$_2$. Activation, using NaO^{t}Bu again gave equal reactivity to the organometallic activator with excellent yield and regioselectivity achieved in the hydroboration of 4-phenyl-1-butene (Table 1, entry 2). Huang reported the catalytic activity of an iron(II) pincer complex, $^{t\text{Bu}}$PNNFeCl$_2$, in combination with NaBHEt$_3$ as the activator for the *anti*-Markovnikov hydroboration of alkenes[11]. Using this iron(II) pre-catalyst and NaO^{t}Bu, in place of NaBHEt$_3$, again gave the linear alkylboronic ester in excellent yield, with exclusive regioselectivity and equal reactivity to that using NaBHEt$_3$ (87%, Table 1, entry 3). Ritter has previously used (imino)pyridine iron(II) dichloride pre-catalysts for the 1,4-hydroboration of 1,3-dienes using activated magnesium as the activator[22]. We further exemplified our activation method by successful application to 6 (imino)pyridine iron(II) chloride pre-catalysts (see SI, Table S3). Using NaO^{t}Bu, the pre-catalyst, $^{i\text{Pr}}$IPFeCl$_2$, loading could be reduced to 1 mol% (from *cf.* 4 mol%) and the 1,4-hydroboration products of myrcene, a naturally occurring terpene, could be synthesised in high yield (93%), on gram-scale, and with equal regioselectivity to that previously reported (Table 1, entry 4).

Table 1| **Iron- and Cobalt-catalysed Hydroboration and Hydrosilylation of Alkenes**



			Previously Reported		This Work
Entry	pre-Catalyst	Substrate	Activator	Yield (%)	Yield (%)[a]
Alkene Hydroboration					
1a	^{Et}BIPFeCl$_2$	1-Octene	Na(Hg)[9]	>98	>95
1b			NaBHEt$_3$[9]	47	
2	^{Et}BIPFeCl$_2$	4-Ph-1-butene	EtMgBr[18]	90	91
3	^{tBu}PNNFeCl$_2$	1-Octene	NaBHEt$_3$[11]	90	87
4	^{iPr}IPFeCl$_2$	Myrcene	Mg*[21]	92 (18:82)	93[b] (20:80)
5	^{iPr}PNNCoCl$_2$	1-Octene	NaBHEt$_3$[12]	>99	>95
6	^{Mes}BIPCoCl$_2$	1-Octene	Co(I)Me[5]	>98	>95
7	TerpyCoCl$_2$	1-Octene	Co(I)Alkyl[6]	87 (59:41)	>95 (93:7)
8	(*S*)-^{iPr}IPO	α-Me-Styrene	NaBHEt$_3$[16]	85 (97% ee)	>95 (98% ee)
Alkene Hydrosilylation					
9	^{Et}BIPFeCl$_2$	1-Octene	Na(Hg)[27]	>98	94[c]
10	^{iPr}PNN^{H}FeBr$_2$	1-Octene	NaBHEt$_3$[14]	90	5
11	^{tBuMe}IPFeCl$_2$	Myrcene	1) ArLi, 2) ^{tBuMe}IP[28]	91 (95:5)	88[d] (92:8)
12	TerpyCoCl$_2$	1-Octene	-	-	68[e] (93:7)
13	^{Et}BIPNiCl$_2$	1-Octene	-	-	48[e]
14	^{Et}BIPMnBr$_2$	1-Octene	-	-	60[e,f]

[a]Reaction conditions: Alkene (0.4 mmol), HBPin (0.44 mmol) or PhSiH$_3$ (0.48 mmol), [Fe] (1 mol%), NaO^{t}Bu (2 mol%), THF (0.5 mL), 25°C, 60 minutes. Yield determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. Regioselectivities are reported in parenthesis as a ratio of linear:branched isomers. [b]0.99 g product isolated. [c]8 mmol scale, *neat*. [d]1.06 g product isolated. [e]Using PhSiH$_3$. [f]Using 2 mol% [Mn] and 4 mol% NaO^{t}Bu.

With the successful activation of over 10 iron pre-catalysts, we were curious whether the NaO^{t}Bu activation could be applied to other earth-abundant metals[24]. Chirik has shown that ^{Mes}BIPCo(I)Me is a

highly efficient pre-catalyst for alkene hydroboration[5], and similarly Huang reported the hydroboration of alkenes using a cobalt(II)-pincer complex, $^{i\text{Pr}}$PNNCoCl$_2$, in combination with NaBHEt$_3$ as the activator[12]. Remarkably, NaO^{t}Bu successfully facilitated pre-catalyst activation for both structurally unique cobalt(II) pre-catalysts, $^{i\text{Pr}}$PNNCoCl$_2$ and $^{\text{Mes}}$BIPCoCl$_2$, to give the alkyl boronic ester in equal yield to that reported previously (>95%) and with complete control of regioselectivity in both cases (Table 1, entries 5,6). Significantly, the activation method was extended to the activation of an enantiopure C_1-symmetric iminopyridine-oxazoline cobalt(II) pre-catalyst $^{i\text{Pr}}$IPOCoCl$_2$, which enabled the hydroboration of α-methylstyrene in excellent yield (95%) and enantioselectivity (98% ee, Table 1, entry 8), once again equalling the reported reactivity using an organometallic activator[16].

Having successfully developed a practical activation method for alkene hydroboration using different ligand structures and metals, we decided to investigate the generality of this method with respect to other reaction classes. Alkene hydrosilylation is one of the largest industrial processes currently in operation[25]. Principally these reactions are carried-out using well-established platinum catalysts, and it is estimated that the global silicones industry consumes *ca.* 5.6 metric tons of platinum annually[26]. As a consequence, several new earth-abundant metal catalysts have emerged for alkene hydrosilylation[20,27,28].

We began by testing the catalytic activity of a range of iron(II) pre-catalysts, in combination with 1-octene and silanes that were compatible with previous methods involving organometallic activators[20]. We quickly found success; a range of bis(imino)pyridine iron(II) pre-catalysts, BIPFeCl$_2$, with varying steric environments were compatible (see SI, Table S5), and we could use $^{\text{Et}}$BIPFeCl$_2$ to catalyse the hydrosilylation of 1-octene with triethoxysilane to give the silylated product in excellent yield (94%) with exclusive linear regioselectivity (Table 1, entry 9). Again, both the high yield and regioselectivity matched that of the analogous state-of-the-art Fe(0) complex[27]. The catalyst scope for alkene hydrosilylation was assessed by application of the activation method to a selection of pre-catalysts with literature-established low oxidation-state catalytic activity (Table 1, entries 9-11). Ritter reported the iron-catalysed 1,4-hydrosilylation of 1,3-dienes using an (imino)pyridine iron(0) species that was

formed by a ligand-induced reductive elimination (C_{sp}^2-C_{sp}^2, bond forming) from a sensitive aryl-ligated iron(II) complex[28]. We therefore applied our novel activation method to the analogous (imino)pyridine iron(II) dichloride pre-catalysts (see SI, Table S3). Using NaO^{t}Bu, the 1,4-hydrosilylation of myrcene was achieved on gram-scale in high yield (88%), and with equal regioselectivity to that previously reported (Table 1, entry 11).

We recognised that if NaO^{t}Bu could be used for the activation of both iron(II) and cobalt(II) pre-catalysts, then the activation of a wide range of traditionally synthetically challenging catalyst systems may also be possible. Specifically, our activation method could be used to discover novel catalytic reaction manifolds. Remarkably, we observed *lead* reactivity from the outset. The cobalt complex TerpyCoCl$_2$, derived from the widely available terpyridine ligand, showed good hydrosilylation activity (Table 1, entry 12). To our surprise, we were unable to find literature precedent for hydrosilylation activity using any analogous terpyridine-cobalt complex. We next targeted nickel(II) and manganese(II) pre-catalysts as there are very limited examples of alkene hydrofunctionalisation reactions with these metals[29-31]. Formation of ^{Et}BIPNiCl$_2$ and ^{Et}BIPMnCl$_2$ followed by application of our NaO^{t}Bu activation method led to the discovery of two entirely novel catalytic manifolds (Table 1, entries 13 & 14). In both cases, successful hydrosilylation to give the *anti*-Markovnikov silane product was achieved with complete regiocontrol in good yields. To the best of our knowledge, this is the first example of a manganese-catalysed alkene hydrosilylation using a manganese(II) pre-catalyst and the first example of hydrosilylation using a bis(imino)pyridine nickel species. These results illustrate the efficacy of the NaO^{t}Bu activation method; not for only the simplification of established methodologies, but also for the discovery of new catalytic processes.

Importantly, we were able to apply the NaO^{t}Bu activation to both iron and cobalt pre-catalysts for hydroboration and hydrosilylation of a series of functionalised substrates without detriment to catalyst activity (Figure 2). Carbonyl functionalities including ester **1a**, ketone **1b** and indole-containing ketone **1d** underwent chemoselective alkene hydroboration using ^{Mes}BIPCoCl$_2$. Sulfonamide **1c** reacted

efficiently without S-N bond cleavage or reduction, and aldimine **1e** was well tolerated using these catalyst activation conditions. Styrene **1f** and derivatives bearing potentially sensitive acetoxy- **1g**, chloro- **1h** and even bromo-substituents **1i** reacted efficiently to give the expected products **2f-2i** in high yields and without detrimental side reactions, such as dehalogenation. Additionally, the iron pre-catalyst ^{Et}BIPFeCl$_2$ could be used for the hydroboration of internal alkyne **1g**, to give (*Z*)-alkenylboronic ester **2g** in good yield. Furthermore, alkene hydrosilylation using the same catalyst, ^{Et}BIPFeCl$_2$, was successful for a number of functionalised alkenes, tolerating fluoro- **1m**, trifluromethyl- **1l** and free amine **1o** groups. We were also able to utilise our activation method to discover the switchable stereoselective hydrosilylation of 1-octyne to give the (*E*)- or (*Z*)-alkenylsilane, **2m** and **2n**, simply by exchanging the metal from Co to Fe, respectively. This wide functional group tolerance, even on base-sensitive substrates, demonstrates the extensive applicability of this activation method, and one that should aid the general progression of base-metal catalysis.

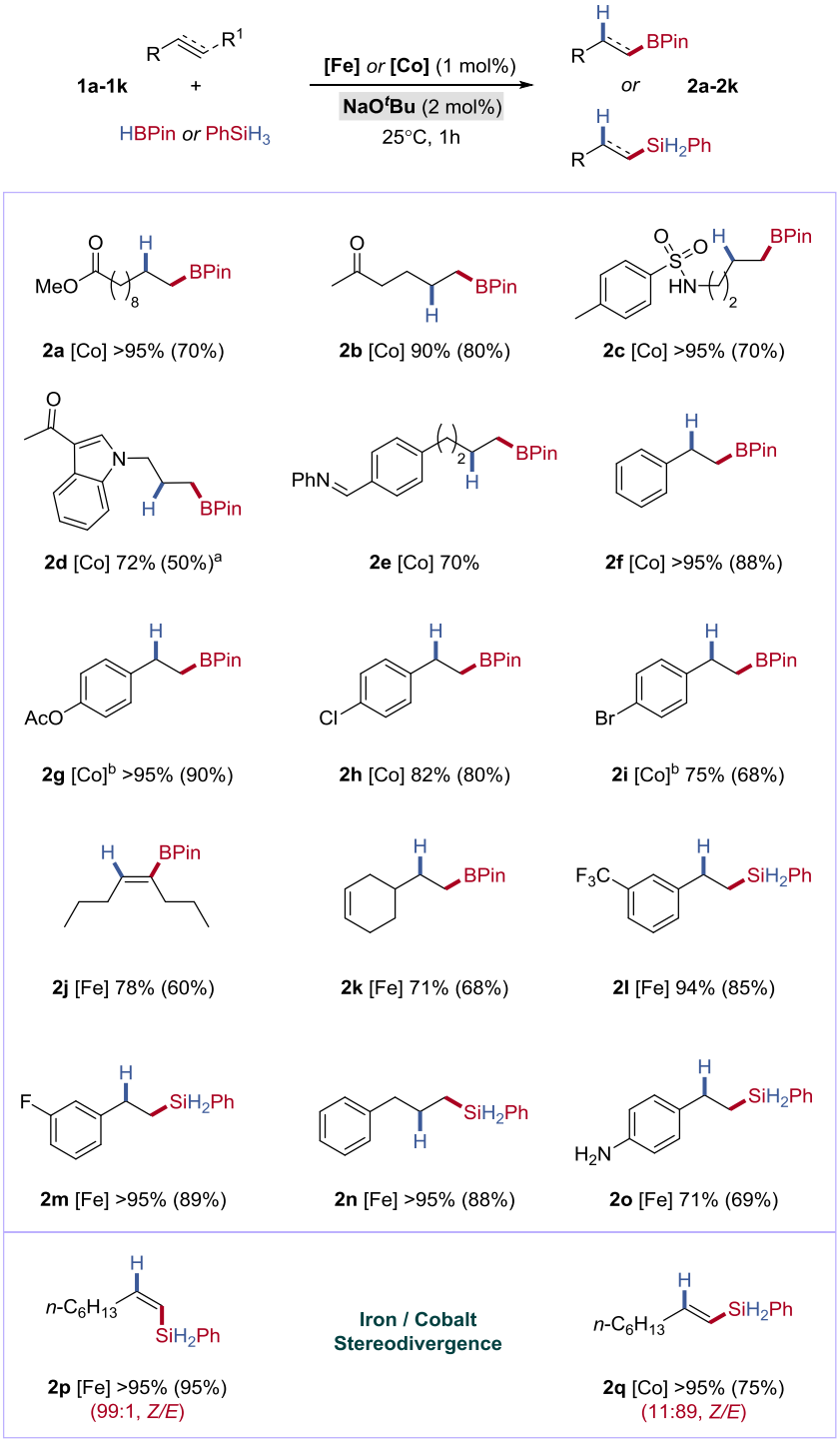


Figure 2| Iron- and cobalt-catalysed hydroboration and hydrosilylation using NaO^{t}Bu as a pre-catalyst activator. Compatibility of iron- and cobalt-catalysts for alkene and alkyne hydroboration (**2a-2k**) and hydrosilylation (**2l-2q**). Yields determined by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard, and Isolated yields are reported in parenthesis. Pre-catalyst used: **[Fe]** = ^{Et}BIPFeCl$_2$, **[Co]** = ^{Mes}BIPCoCl$_2$, **[Co]^b** = ^{iPr}PNNCoCl$_2$ (see supporting information for experimental details). [a]Yield of isolated product following oxidative work-up.

Isolated low-oxidation state formal iron(0) complexes have been shown to offer catalytic activity that surpasses that of conventional platinium-catalysts for alkene hydrosilylation[27]. Therefore, it was important to assess the effectiveness of our activation method for the generation of active catalysts in industrially relevant situations. We targeted the hydrosilylation of 1-octene with triethoxysilane, a commercially relevant silane, as there was a comparable example for this using an analogous 'iron(0)' complex. Using NaO^{t}Bu and ^{Et}BIPFeCl$_2$, we were able to achieve equal reactivity to the state-of-the-art complex, {[^{Et}BIPFe(N$_2$)]$_2$(μ_2-N$_2$)}, with even lower catalyst loadings than had previously been reported (Figure 3).

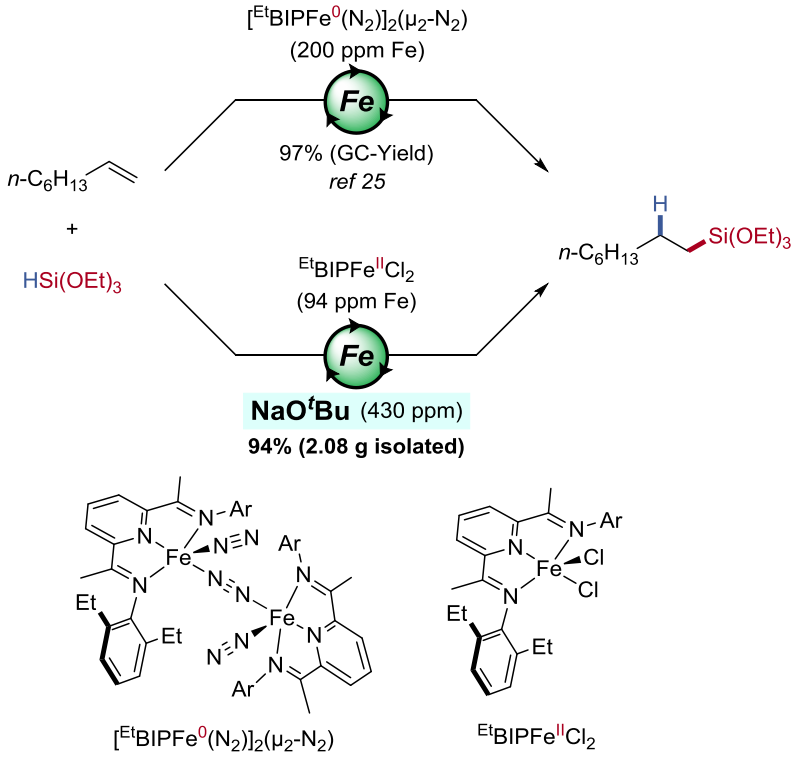


Figure 3| Gram-scale hydrosilylation using a ppm quantity of iron (pre-)catalyst – state-of-the-art iron(0) reactivity compared to NaO^{t}Bu activation method.

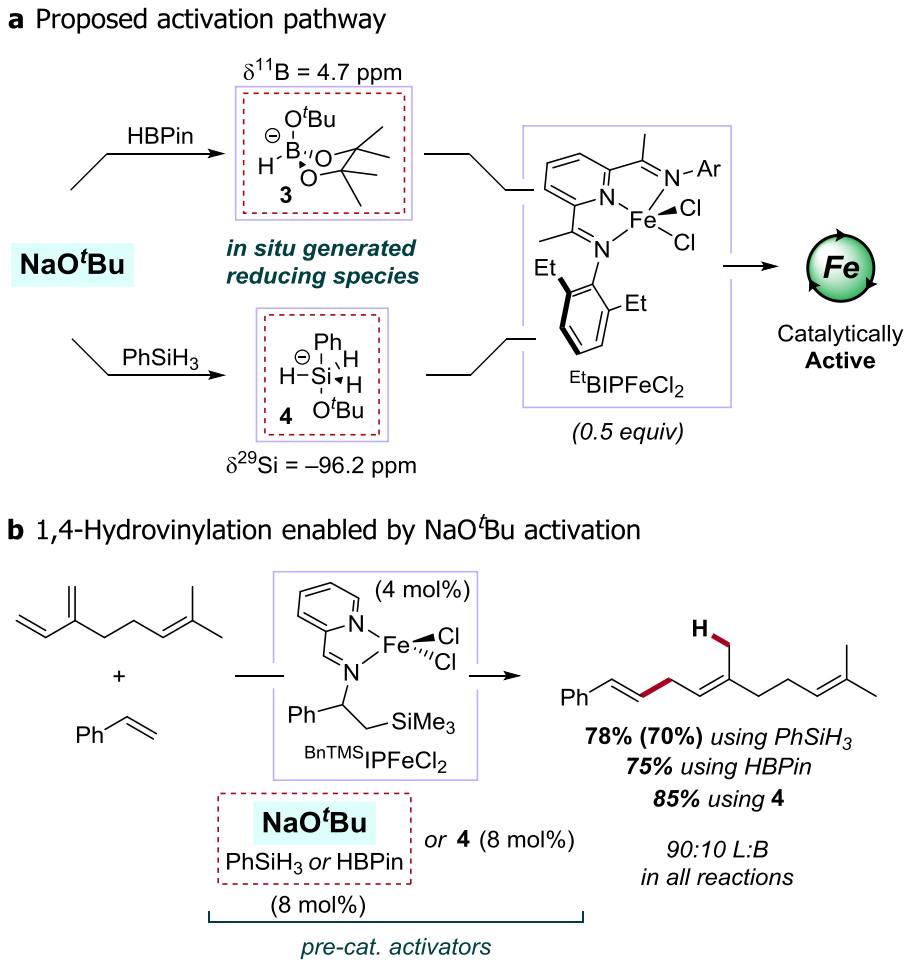


Figure 4| **a** Proposed pre-catalyst activation pathway, by formation of boron 'ate' species **3** or silicon 'ate' **4**. **b** 1,4-Hydrovinylation of myrcene, using an iminopyridine-iron pre-catalyst activated by sub-stoichiometric quantities of phenylsilane and sodium *tert*-butoxide. **c** Alkene hydrogenation by *in-situ* generated active catalysts using silicon 'ate' **4** reduction. **d** Alkene [2π+2π] cycloaddition, previously accessed using sensitive low-oxidation state pre-catalysts, enabled by *in-situ* formation of active species using silicon 'ate' **4**.

Mechanistically, the NaO^{t}Bu activation proceeds by reaction of the alkoxide with the boronic ester or silane to form an 'ate' species which activates the metal pre-catalyst by, presumably, hydride transfer and reductive elimination. Stoichiometric reactions of NaO^{t}Bu and HBPin produced the boron 'ate' complex **3** (see SI)[32]. Similarly reaction of phenylsilane ($PhSiH_3$) with NaO^{t}Bu resulted in the observation of a penta-coordinate silicon 'ate' species **4**. Addition of this mixture to the iron pre-catalyst, ^{Et}BIPFeCl$_2$, resulted in the formation a mixture of paramagnetic iron species which demonstrated high catalytic reactivity (see SI for experimental details). Given that we could access an active catalyst using **4**, we realised that either: a) boron 'ate' complex **3**, b) silicon 'ate' complex **4**, or alternatively c) substoichiometric quantities of silane or borane and *tert*-butoxide could potentially be used as general pre-catalyst activators to enable reactions outwith hydroboration and hydrosilylation. Therefore, we targeted hydrovinylation[33], hydrogenation[2,17] and alkene [2π+2π] cycloaddition reactions[34,35] in an effort to demonstrate general accessibility to low oxidation-state catalyst manifolds.

Reaction of myrcene with styrene using the *in situ* generated catalyst, from ^{BnTMS}IPFeCl$_2$, produced the anticipated 1,4-hydrovinylation products in excellent yield and regioselectivty when using either HBPin or $PhSiH_3$ (Fig. 4b). Additionally, we used **4** as an *in situ* activator for a selection of iron and cobalt pre-catalysts which enabled alkene hydrogenation in high yield (Fig. 4c). Similarly, $^{i\text{Pr}}$BIPFeCl$_2$ and $^{i\text{Pr}}$BIPCoCl$_2$ could be activated using **4**, to catalyse the intramolecular [2π+2π] cycloaddition reaction which was previously only reported using isolated low oxidation-state (Fe^0 and Co^I) pre-catalysts (Fig. 4d).

Conclusions

In summary, an easily handled, air- and moisture-stable alkoxide salt could be used for the activation of a wide-range of non-precious metal pre-catalysts. State-of-the-art low oxidation-state iron- and cobalt-catalysed manifolds, previously only accessible using strict air/moisture-free techniques, were realised in the simplest manner and opened to the non-expert. Most notably, using the NaO^{t}Bu activation approach, novel cobalt(II)-, manganese(II)- and nickel(II)-catalysed alkene hydrofunctionalisation reactions were discovered. Mechanistic investigations show that NaO^{t}Bu acts as

a *masked* reducing agent, by forming an 'ate' species with HBPin or silanes that serve as pre-catalyst activators. The simplicity and generality of this method provides a platform for the development and exploitation of non-precious metal catalysis.

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Contributions

J.H.D and S.P.T. conceived and discovered the NaO^tBu activation. J.H.D and J.P conducted the experimental work. S.P.T and A.D advised investigations. J.H.D and S.P.T prepared the manuscript.

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